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**MONSANTO/WASHINGTON UNIVERSITY
ONR/ARPA ASSOCIATION**

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CONTENT OF PLASTIC COMPOSITES**

By
W. M. HAYNES AND T. L. TOLBERT

**PROGRAM MANAGER
ROLF BUCHDAHL**

JANUARY 1970

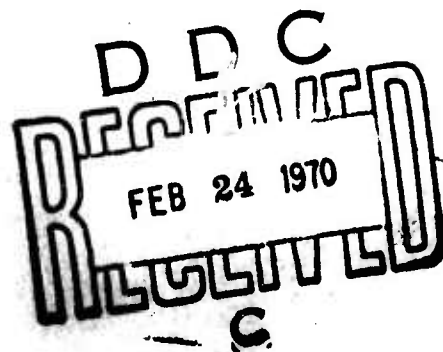
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HPC 68-81

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BY
W. M. HAYNES AND T. L. TOLBERT

JANUARY 1970

MONSANTO/WASHINGTON UNIVERSITY ASSOCIATION
HIGH PERFORMANCE COMPOSITES PROGRAM
SPONSORED BY ONR AND ARPA
CONTRACT NO. N00014-67-C-0218, ARPA ORDER 876
ROLF BUCHDAHL, PROGRAM MANAGER

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FOREWORD

The research reported herein was conducted by the staff of the Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

The prime contractor is Monsanto Research Corporation. The Program Manager is Dr. Rolf Buchdahl (Phone-314-694-4721).

The contract is funded for \$6,000,000 and expires 30 April 1971.

A RAPID DETERMINATION OF THE GRAPHITE FIBER CONTENT OF PLASTIC COMPOSITES

W. M. Haynes and T. L. Tolbert

The recent advent of graphite fiber as a practical reinforcing agent for plastic composites has greatly increased the need for a rapid, accurate method for determining the exact amount of this fiber present in composite specimens. The traditional method of determining fiber content by ignition loss in glass fiber reinforced composites (often used in boron fiber composites, as well) is not practical for graphite fiber systems because of oxidative-sensitivity of the graphite. The host of laboratory procedures based on solvent extraction of dissolved resin tends to be too slow and cumbersome to be effective or economical for routine quality control applications, particularly when the resin is a thermoset. The more recent acid digestion methods are definite improvements, but also tend to be slow and usually require a high level of operator training to prevent handling losses. One of the better of these, a method developed by Kuhbänder (1) calls for three two-hour treatments with concentrated nitric acid followed by a distilled water rinse, drying the remaining material for two hours and final weighing. In addition to the error caused by carbon losses during the long acid treatment, the physical handling of the graphite in the four filtration steps and during weighing offers opportunity for additional error.

Research was consequently undertaken to develop a rapid, quantitative analytical procedure which would minimize the problems of the earlier methods and be suitable for production control. The method described in this paper is the result. It allows the graphite fiber content of epoxy and polyimide resin composites to be determined in as little as one and a half hours. Only two and a half hours are required for the determination in phenolic-based systems.

Experimental Methods

A 0.3 to 0.5 gram sample of the composite in question is weighed into a 300 ml. tall form beaker, care being taken to avoid resin loss due to crazing or flaking during preparation of the sample (it should be noted that since this is a gravimetric technique, the larger the sample taken, the less are sampling errors* and the error of weighing). To this are added 20 mls. of concentrated sulfuric acid. It is not necessary to grind the sample in any way. After addition of the sulfuric acid, the mixture is placed on a hot plate and heated until the acid begins to fume. The composite will begin to visibly disintegrate as soon as the acid is hot, with resin particles and fibers

*Sampling errors due to resin flaking may be reduced by cutting specimens with a high speed, diamond blade saw or, in the case of unidirectional composites, by splitting of specimens in the direction parallel to the fibers (rather than breaking the composite across fibers).

dispersing throughout the sulfuric acid solution. Hydrogen peroxide (50%) is then carefully added dropwise down the side of the beaker. The addition is made slowly at first in order to prevent splattering of the mixture, but the rate of addition may be increased as the reaction proceeds. Rubber gloves and a fume hood with appropriate safety glass shield should be used throughout the addition. In all cases, precautions should be taken to handle the hydrogen peroxide as recommended by the Analytical Methods Committee (2).

As the polymer is oxidized, the graphite fibers will rise to the top of the sulfuric acid solution. The reaction is considered complete when the hot sulfuric acid solution below the fibers becomes clear and colorless. An additional two milliliters of hydrogen peroxide is added to the solution at this point and the solution is heated to fumes for another 10 minutes to ensure complete decomposition of the polymer. The beaker is removed from the hot plate, allowed to cool to about 70° to 80° and then placed in an ice bath. The graphite fibers are collected by vacuum filtration through a medium porosity sintered glass crucible. After the sulfuric acid has been filtered off, the fibers in the crucible are washed thoroughly with 600 mls. of distilled water, added a few milliliters at a time. This washing usually removes the last traces of sulfuric acid, but this should be verified by checking the pH of the last drops of filtrate. Washing should be continued until the filtrate is no longer acidic. The fibers are then rinsed with

absolute ethanol to remove surface moisture. The crucible is removed from the filtering system, placed in an open beaker, and dried in an oven at 140°-150°C. for 45 minutes. After drying, the crucible is cooled in a desiccator and weighed. The difference between the crucible weight and the weight of the crucible plus sample is the weight of the graphite fibers. The weight percent and volume percent of the fibers present in the original sample can then be calculated using the weight of the graphite fibers, sample weight, and the appropriate densities of the matrix resin and the graphite fibers.

Results

Preliminary studies were made with Thronel 50 Graphite yarn purchased from Union Carbide Corporation to determine if such material is appreciably oxidized during digestion. The yarn showed no significant loss in weight after treatment with sulfuric acid or 50% hydrogen peroxide (FMC Corporation, Buffalo, N.Y.), added individually or in combination. In contrast, a 0.3 gram sample of an epoxy matrix resin was found to completely dissolve in as little as 3 minutes. With composites of graphite fiber in epoxy resin, a longer digestion time was allowed to insure complete destruction of the polymer. Four samples of high performance graphite fiber-epoxy composites were analyzed in duplicates. (Only duplicates were run in this

particular case due to lack of samples).

Epoxy Composites

w/o Graphite Fiber (Expected) *		w/o Graphite Fiber (Analyzed)	
		A	B
1.	38.0	38.1	37.9
2.	38.0	38.2	37.6
3.	38.5	38.3	38.9
4.	39.0	39.2	39.4

*Approximate fiber loading based on the quantity of materials used.

Polyimide composites were also analyzed. Standards were prepared by carefully weighing granulated, "B" staged Skybond 700 (Monsanto Company) resin and Thornel WYF-130 graphite yarn into a 1" x 1" mold and processing the mixture at 175°C and 500 lb. pressure according to the procedure recommended by the manufacturer to form a composite. Care was taken to completely remove all of the composite from the mold so that the entire sample could be digested and analyzed.

Polyimide Composites

w/o Graphite Fiber (Standard)		w/o Graphite Fiber (Analyzed)
1.	26.6	26.5
2.	31.4	32.0
3.	47.2	46.9

In addition, graphite fiber reinforced composites based on phenolic matrices and on thermoplastic resins such as the polycarbonates and polysulfones can be readily analyzed by this technique.

Conclusion

The analytical technique described in this paper provides a rapid determination for the graphite fiber content of composites based on epoxy, polyimide and phenolic resins. This method also can be used to determine the void content of such composites. It should be noted that the method is not acceptable for glass or asbestos filled composites due to the attack of glass and asbestos by concentrated sulfuric acid.

Acknowledgments

The authors wish to thank Mr. J. D. Ray, Plastics and Composites Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, for his interest and for providing specially selected experimental specimens of known fiber content which could be used in further verifying the accuracy and flexibility of the described technique.

The work described in this paper was performed by the Monsanto/Washington University Association sponsored by the Advanced Research Projects Agency, Department of Defense, under Office of Naval Research Contract No. N00014-67-C-0218, formerly N00014-66-C-0045.

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1. R. J. Kuhbander, "Determining Fiber Content of Graphite Yarn-Plastic Composites," AFML-TR-67-243.
2. Analytical Methods Committee, "The Use of 50 Per Cent Hydrogen Peroxide for the Destruction of Organic Matter," Analyst, Vol. 92 (1967), pp. 403-407.

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION	
Monsanto Research Corporation		Unclassified	
		2b. GROUP	
3. REPORT TITLE			
A Rapid Determination Of The Graphite Fiber Content Of Plastic Composites			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
5. AUTHOR(S) (First name, middle initial, last name)			
W. M. Haynes and T. L. Tolbert			
6. REPORT DATE		7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
January 1970		14	2
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S)	
N00014-67-C-0218		HPC 68-81	
b. PROJECT NO.			
c.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT			
This document is subject to special export controls and each transmittal to foreign governments or foreign nations may be made only with prior approval of the Director of Material Sciences, Office of Naval Research.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
		Office of Naval Research Washington, D. C. 20360	
13. ABSTRACT			
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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Graphite fiber Plastic composites Reinforcing agent Quantitative analytical procedure Epoxy Polyimide resin Gravimetric Technique Sulfuric acid Hydrogen peroxide (50%) Thornel 50 Graphite yarn Skybond 7000 Resin Thornel WYF-130 graphite yarn rapid determination void content						